Quartz and Magnetite: Oxygen-18-Oxygen-16 Fractionation in Metamorphosed Biwabik Iron Formation

Abstract. *Oxygen-18–oxygen-16 fractionation of coexisting quartz and magnetite from the Biwabik iron formation varies as a function of distance of the sample from an intrusive contact. This isotope fractionation is related to observed mineralogic variations and compared with a theoretical heat-flow model.*

The Biwabik iron formation extends in a 190-km belt east-northeast across northern Minnesota (*1*). The rocks of the western segment of this belt are composed primarily of quartz, magnetite, siderite, minnesotaite, greenalite, stilpnomelane, and some chamosite and hematite, all of which are commonly less than 0.1 mm in maximum dimension. The iron formation displays complex layering on a scale ranging from less than a millimeter to a few centimeters; this layering consists predominantly of quartz-rich material alternating with material rich in magnetite, siderite, or iron silicates.

The eastern 25-km segment of the iron formation has been metamorphosed by the Duluth gabbro complex. Here, the iron formation crops out from 0 to 6 km north of the southward dipping basal contact of the gabbro. The iron formation dips 5° to 30° southward, beneath the gabbro. Thus the projected minimum distance between the two, prior to erosion, is a few hundred meters or less. The metamorphosed iron formation consists predominantly of quartz and magnetite with abundant grunerite-cummingtonite, ferrohypersthene, hedenbergite, fayalite, hornblende-actinolite, and some garnet, diopside, wollastonite, idocrase, calcite, pyrrhotite, graphite, and hematite. Within a true distance (*2*) of about 150 meters from the gabbro much of the magnetite and all of the quartz have become coarsely crystalline. Magnetite grains commonly range up to 1 mm, and much of the quartz occurs in grains 1 to 5 mm in maximum dimension.

Table 1. Isotopic composition of oxygen in quartz and magnetite from samples of Biwabik iron formation.

Sample No.	δ Quartz (per mil)	δ Magnetite (per mil)	Mean* deviation (per mil)	1000 ln α_{Q-M}	Distance from gabbro contact (km)
32-64	13.63	6.43	± 0.08 (2) ± .06 (2)	7.1	0.48
6-64	17.25	5.13	(1) (1)	12.0	1.85
5-64	12.11	2.21	± .01 (2) (1)	9.8	2.25
7-64	16.31	0.62	± .05 (2) (1)	15.6	2.81
2-64	17.03	−2.10	(1) (1)	19.0	2.97
25-64	18.35	−3.78	(1) (1)	22.0	16.0
19†	16.4	7.2		9.1	~1.6
20†	14.4	5.3		9.0	~2.4

* Numbers in parentheses indicate number of determinations. † From reference (*5*), distances approximate.

Table 2. Isotopic composition of oxygen in quartz and magnetite from precisely located samples of Biwabik iron formation.

Sample No.	δ Quartz (per mil)	δ Magnetite (per mil)	Mean* deviation (per mil)	1000 ln α_{Q-M}	True distance from gabbro contact (meters)
M12056	15.21	7.43	(1) ± 0.15 (4)	7.7	15
M12022	12.91	4.69	± 0.01 (2) ± 0.10 (5)	8.2	52
M12133	12.45	4.95	(1) ± 0.02 (3)	7.4	63
M12067	12.64	4.49	(1) (1)	8.1	70.8
M12167	13.09	4.22	(1) ± 0.23 (4)	8.8	102
M12232	13.98	5.49	(1) ± 0.10 (2)	8.4	128
36-64	18.90	9.28	(1) (1)	9.5	154
37-64	12.53	2.49	± 0.05 (2) ± 0.01 (2)	10.0	171
38-64	14.10	2.53	± 0.07 (2) ± 0.05 (2)	11.5	210

* Numbers in parentheses indicate number of determinations.

As part of a detailed study of oxygen-isotope exchange in the iron formation we have determined the O^{18}/O^{16} fractionation between quartz and magnetite adjacent to the gabbro. O'Neil and Clayton (*3*) have experimentally demonstrated that a large equilibrium isotopic fractionation between quartz and magnetite exists and that this fractionation decreases with increasing temperature. It seems desirable to test this "geothermometer" in a metamorphic aureole of relatively simple structure and mineralogy. Furthermore, an accurate temperature profile of the metamorphosed Biwabik iron formation beneath the Duluth gabbro may give added significance to petrologic studies like those of French (*4*). A broad survey of oxygen isotopic fractionation in this and other iron formations has been made by James and Clayton (*5*).

Oxygen was extracted from separated samples of coexisting quartz and magnetite by the BrF_5 technique (*6*). Most mineral separates were visually estimated to be more than 98 percent pure. With a few very fine-grained samples, mineral separates 95 to 98 percent pure were used. No corrections for impurities have been made. Oxygen yields for quartz were 100 percent. For magnetite, yields ranged from 85 to 100 percent; no detectable error was introduced by using magnetite samples with oxygen yields in this range. Isotopic analyses were performed on a 6-inch (15-cm) mass spectrometer with a double ion-beam collector, similar to that described by McKinney *et al.* (*7*).

Almost all samples used in this study were taken from small volumes within mineralogically homogeneous laminae. This sampling technique was chosen in an effort to maximize the probability of obtaining assemblages in local isotopic equilibrium at the highest temperature of metamorphism. A concurrent uncompleted study (*8*) indicates that local isotope gradients attributable

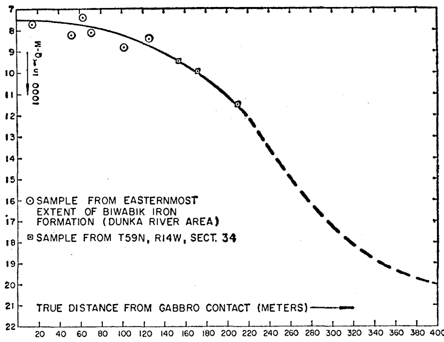

Fig. 1. Relation of oxygen isotope fractionation between quartz and magnetite to true distance (*2*) from Duluth gabbro contact.

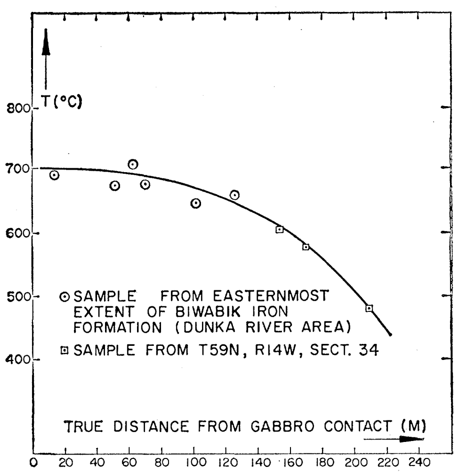

Fig. 2. Relation between temperature (inferred from reference *3*) and true distance from the Duluth gabbro contact (*2*).

to both prograde and retrograde metamorphism are observable in the most highly metamorphosed iron formation. This suggests that isotopic equilibrium was approached within a given small system at the temperature maximum for that system. The magnitude of the retrograde gradient suggests that, near the contact, measured oxygen isotopic fractionations between quartz and magnetite may be about one unit too high to correspond to maximum temperatures of metamorphism (*9*).

Table 1 lists oxygen isotope data from a reconnaissance study of the eastern part of the Biwabik iron formation. There is an abrupt change in oxygen isotope fractionation between 2 and 3 km from the contact. This may be compared to the rapid series of mineralogical changes reported by French (*10*) in the same distance interval.

Because the metamorphic aureole produced by the Duluth gabbro is quite narrow, it is possible to observe significant systematic variations in fractionation within the cores of drill holes which extend through the gabbro into the underlying iron formation or which are located so close to the basal gabbro contact that this contact can be accurately projected. Data from these cores are given in Table 2. In Fig. 2, 1000 ln α_{Q-M} is plotted versus true distance of the sample from the gabbro (*2*).

Two things may be noted about Fig. 2. First, the gabbro contact intercept of the quartz-magnetite fractionation is 7.5, which corresponds to an experimentally measured temperature of approximately 700°C (*3*). Arbitrarily subtracting 1.0 for retrograde metamorphism would increase this temperature to about 750°C. This is a rather high contact temperature (*11*) and it lies in the most accurately determined portion of the experimental system. Also, $d \ln \alpha_{Q-M}/dD$ is small near the gabbro contact intercept and becomes larger at some distance from the intercept. Fig. 2 shows that a temperature-distance plot with temperatures taken from O'Neil and Clayton (*2*) would have the same shape. These curves are convex in the opposite sense to that predicted for the intrusion and cooling of a simple tabular body (*11*). Such a shape and contact temperature might result from the periodic addition of heat to the system over an interval of time rather than in a single brief episode.

Our work suggests that quartz-magnetite fractionation can yield valuable information about the physical conditions under which metamorphic rocks formed, even though retrograde effects are by no means negligible. If the anomalous shape of Fig. 2 results from repeated addition of heat to the system, a direct comparison between Jaegers' model (*11*) and Fig. 2 of the distance at which the temperature has dropped to half its contact value should result in a maximum estimate of the thickness of the marginal portion of the Duluth gabbro complex. Such an estimate gives a value on the order of 500 meters.

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References and Notes

1. F. F. Grout, and T. M. Broderick, *Minn. Geol. Surv. Bull.* No. 17 (1919); J. W. Gruner, "The mineralogy and geology of the taconites and iron ores of the Mesabi Range, Minnesota," *Iron Range Res. Rehabilitation*, 1946 (Minnesota Geological Survey, Minneapolis, 1946); D. A. White, *Minn. Geol. Surv. Bull.* No. 38 (1954); J. N. Gundersen and G. M. Schwartz, *Minn. Geol. Surv. Bull.* No. 43 (1962).
2. True distance is used to mean perpendicular distance from the sample to the plane of the gabbro contact.
3. J. R. O'Neil, and R. N. Clayton in *Isotopic and Cosmic Chemistry* (North-Holland, Amsterdam, 1964).
4. B. M. French, *Science* **146**, 917 (1964); thesis, Johns Hopkins University.
5. H. L. James and R. N. Clayton in *Petrologic Studies, Buddington Volume*, A. E. J. Engel, H. L. James, B. F. Leonard, Eds. (Geological Society of America, New York, 1962), pp. 217–233.

R. N. Clayton and T. K. Mayeda, *Geochim. Cosmochim. Acta* **27**, 43 (1963).

7. C. R. McKinney, J. A. McCrea, S. Epstein, H. A. Allen, H. C. Urey, *Rev. Sci. Instr.* **21**, 724 (1950).
8. E. C. Perry and B. Bonnichsen, Abstr. in *Trans. Amer. Geophys. Union* **47**, 212 (1966).
9. We have expressed fractionation as 1000 $\ln\alpha_{Q-M}$ where $\alpha_{Q-M} = (O^{18}/O^{16})_Q/(O^{18}/O^{16})_M \simeq \delta_Q - \delta_M$. The quantity δ is defined as
$$\left(\frac{(O^{18}/O^{16})_{\text{sample}}}{(O^{18}/O^{16})_{\text{standard}}} - 1\right)(1000).$$
The standard for this study is standard mean ocean water [H. Craig, *Science* **133**, 1833 (1961)].
10. French (*4*, fig. 79 in thesis). Our sample control is not adequate to give accurate quartz-magnetite isotope fractionations corresponding to French's tightly spaced isograds. Tentative values are: (i) appearance of ferrohypersthene and of crystalline graphite, 10; (ii) appearance of hedenbergite, 15; (iii) appearance of grunerite, 18.
11. J. C. Jaeger, *Amer. J. Sci.* **255**, 306 (1957).
12. Support from NSF grants GP 366, GP 2861, and GP 5071. H. L. James suggested the problem. Erna Beiser made most of the mass spectrometric determinations.

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Shallow Structure of the Straits of Florida

Abstract. *Continuous seismic profiles of the Straits of Florida indicate that north of 26°30'N the trough was formed mainly by sediment upbuilding along the margins. South of this latitude the straits may be due in part to faulting.*

The Florida peninsula is located on the eastern margin of a broad submarine platform known as the Florida Plateau (*1*). To the east and south of the Florida Plateau is the Straits of Florida, an arcuate trough 700 km long and 90 to 145 km wide (Fig. 1). Depths along the axis of the Straits of Florida range from 2200 m south of Dry Tortugas to 740 m west of Little Bahama Bank.

Structural and erosional origins have been postulated for the Straits of Florida and the other troughs in the Florida-Bahama region. Agassiz (*1*) suggested that submarine erosion by the Gulf Stream was responsible for the formation of the Straits of Florida. Hess (*2*) interpreted the troughs in the Bahamas as drowned river valleys and the banks between the troughs as having been formed by upgrowth of reefs